

Description of WO03030289	<u>Print</u>	<u>Copy</u>	<u>Contact Us</u>	<u>Close</u>
--------------------------------------	---------------------	--------------------	--------------------------	---------------------

Result Page

Notice: This translation is produced by an automated process; it is intended only to make the technical content of the original document sufficiently clear in the target language. This service is not a replacement for professional translation services. The esp@cenet® Terms and Conditions of use are also applicable to the use of the translation tool and the results derived therefrom.

Polymers gas cell membrane and method to its production the invention refer to the fields power generation, construction of vehicles and chemistry and concern polymere gas cell membranes, like it for example into direct methanol fuel cells to the use to come can and a method to their production.

An important role in low temperature fuel cells such as z. B. the fuel cells operated with hydrogen or the direct methanol fuel cells (English. Direct methanolFuel Cell; DMFC) comes to the polymer electrolyte membranes (PEM). The object is to separate on the one hand the two electrode areas and minimize the methanol permeability as well as on the other hand proton transport between the anode compartment (in that the hydrogen to protons and/or. Methanol to protons and carbon dioxide oxidized will ensure) and the cathode compartment (in the oxygen reduced becomes). The minimization of the methanol permeability is required, since the reaction of methanol with oxygen in the cathode compartment leads to a reduction of the efficiency.

The requirements to the PEM for the use in fuel cells are the subsequent: 1. high chemical and electrochemical stability, in particular more bottom

Operating conditions

2. high mechanical stability during the operation 3. Guarantee of a good and permanent adhesion to the catalyst

4. extreme small permeability for reactants, around high Coulomb

To place effectiveness safer

5. high electrolyte transport (water) around an uniform distribution in that

To ensure membrane and to avoid a " local " draining

6. high proton conductivity to the support of high current densities with small Ohm' resistances

7. no electron conductivity by the membrane

8. Product costs, which are the respective application adequate.

A revue over used polymers as membranes in the gas cell technology became from O. Savadogo given (O. Savadogo, journal OF

New material for Electrochemical of system 1.47-66 (1998)).

Due to its excellent chemical stability and electric

Properties (proton conductivity) became so far cation exchanger membranes on the basis of perfluorinated hydrocarbons, which became first for the chlorines alkali electrolysis developed, in fuel cells used. The proton conductivity becomes achieved by sulfonic acid groups in the side chains of these polymers. Such membranes are the bottom trade name Nation@ (DuPont), DowMembran (Dow Chemical), FlemionG (Asahi Glass of cost, Ltd.) and AciplexS (Asahi Chemical Industry of cost, Ltd.) known.

A major disadvantage of these membranes is their high price (approx. 800 US \$/m²). An other disadvantage is their methanol permeability in particular with higher methanol concentrations, so that the fuel cells not bottom optimum conditions operated to become to be able. Furthermore these membranes dry with operating temperatures > 100 C out, which leads to a reduction of the Protonenleiffähigkeit. Nevertheless these temperatures become z. Time. as necessary regarded, in order to ensure a rapid desorption of the CO from the catalyst to, which also develops during the oxidation of methanol and represents a catalyst poison.

Strengthened membranes on the basis of ptfe microfiltration diaphragms, which became with a perfluorinated more lonomer coated, are also known (fermenting SELECT, And Associates would ferment; US 5, 547, 551). This technology the permitted production of thinner

Membranes, which leads to a reduction of the Ohm' resistance. The proton conductivity is however smaller than those specified the above nation or Dows membranes.

The use of A, ss, ss-Trifluorstyrolsulfonsäure-copolymers as Membrane materials in fuel cells z became. B. of ball pool of broadcasting corporations described (US 5,422, 411). These materials point compared with the analogous, not-fluoridated Polymers a significant higher oxidation stability up. In hydrogen Fuel cells exhibit these membranes better electrical properties as nation or Dows membranes.

The grafting of fluoridated and unfluoriertem polystyrene on ptfe or other fluoridated support materials and additional sulfonation became described in various publications (US 4.012, 303; US 4, 166, 014; US 4, 506,035; US 4.605, 685). This method results in in particular in the case of the use of unfluoriertem styrene membranes with smaller conductivity than Nafion or Dows membranes and membranes with small chemical stability (oxidative degradation).

Membranes from Polybenzimidazol became described (B. Cahan, J. S. Wainright, J.

Electrochem. Soc. 140, L185 (1994); P. Staiti, M. Minutoli, S. Hocevar, J. Power SOURCES 90.231-235 (2000)). These membranes must become with phosphoric acid, Polywolframsäure or phosphorus-tungsten-acidic impregnated, in order to reach a proton conductivity. The acidic one

becomes bottom salt formation with the Imidazolgruppen polymers to the matrix of the bound. The ratio imidazole to acidic ones lies in the order of magnitude 1: 3 to 1: 5. With these materials however the danger exists that the acidic one is delivered by waters from the membrane, formed during the operation, and thus the proton conductivity lost goes.

Sulfonated Polyarylethersulfon (PES, PSU) became described as membrane material for PEM (C. Arnold, R. A. ASS ASS, J. Diaphragm Sci. 38, 71 (1988)).

Sulphonation degrees over 29,5% lead to water-soluble products.

Sulphonation degrees to 29% give products, which are in hot water soluble.

Further pour these materials very strong, which to poor mechanical Properties leads. Crosslinked sulfonated polyethersulfones exhibit a smaller swellable, however the specific conductivity decreases compared with the uncrosslinked products around the factor 2.

In EP 0,574,791 a2 sulfonated Polyetheretherketon (PEEK) becomes as Membrane material for the use in fuel cells described. High sulphonation degrees, which are necessary for a sufficient proton conductivity, lead however to Materialien with high degrees of expansion and thus poor mechanical properties (shortening of the life of the membrane). With inhomogeneous sulfonated PEEK the danger of the embrittlement exists by recrystallization, since PEEK is part-crystalline.

The use of Blockcopolyimiden from sulfone-acidic segments and not-sulfonated segments as membrane material became 96/05707 described in FR. These membrane materials became so far only in hydrogen/oxygen fuel cells tested, which makes an estimate of the suitability of these materials in DMFC difficult.

Of Kerres et al. became Polyionenkomplexmembranen on the basis of Polybenzimidazol, polyethyleneimine, aminated polysulfone or Poly (4-vinylpyridin) (of basic polymers) and sulfonated polysulfone (sPSU) and/or. sulfonated Polyetheretherketon (sPEEK) (acidic polymers) described (J. Kerres, A. Ullrich, T.

Hectar ring, M. Baldauf, And. Gebhardt, W. Preidel; Journal OF of new material for Electrochemical of system, 3.229-239 (2000)), those in hydrogen/oxygen fuel cells significant better electrical properties as Nafion[®]; - 117 exhibit. If these membranes in DMFC become tested with different methanol concentrations, then only slight differences point themselves in the electric behavior to the Nafion-117 membrane.

A major drawback of all known polymeric membranes for fuel cells are the insufficient mechanical stability and/or the insufficient methanol support ability.

The object of the instant invention is it, a polymere fuel cells
To indicate membrane, which exhibits an improved mechanical stability and/or a substantially improved methanol support ability.

The invention is in the claims indicated. Developments are subject-matter of the
Unteransprüche.

With the instant invention polymere becomes gas cell membranes provided, which can eliminate existing lacks of the state of the art.

The polymere gas cell membranes according to invention can consist several separate-active layers of or. It is also possible that or several carrier is a present. As carriers materials come to the use, which prevent the function of the separate-active layer (EN) at least not complete -or, favourable-prove support it the function of the separate-active layer (EN). Or several separate-active layer (EN) on a carrier an applied can be, it can the separate-active layer (EN) between two carriers disposed be, it can the material of the separate-active layer (EN) also for example in voids, pores of a support material applied be.

Combinations of these possibilities are likewise realizable. The carrier is to ensure and/or increase the mechanical stability of the membrane mainly. Favourable way is it from a textile or a porous material constructed.

The separate-active layer according to invention consists multi-block copolymer with one of the general segment structures A (B A) of at least a Diund/or k and/or B (A-B), and/or (A-B) m with $k \geq 1$ and $1 \leq m$. These segment structures can be present in a multi-block copolymer also simultaneous next to each other and in different numbers. The Diund can be/or multi-block copolymers linear or branched formed.

Further according to invention the block segments (A) and (B) consist in each case of Oligomersegmenten, whereby the block segment (A) from at least one Electron-non conductive and proton-non conductive Oligomersegment, and that Block segment (B) from at least a proton-conductive and electrons non conductive Oligomersegment constructed is.

As oligomers compounds become referred to the state of the art, which consist of a small number of monomerer molecules. One calls it Dimere, Trimers, tetramers etc. (Stoeckhert, Kunststofflexikon 9. Edition, Carl Hanser Publishing house Munich Vienna 1998). Exhibit the oligomers favourable-proves degrees of polymerization from 2 to 50.

The present oligomers, both of the block segment (A) and of

, Can consist block segment (B) in each case of same or various Oligomereinheiten, whereby (A) and (B) the same Oligomereinheiten do not exhibit. The length in particular the block segment (B) should favourable-proves after an optimum proton conductivity selected to become.

In each case the membrane according to invention must exhibit a morphologic structure with essentially continuous proton conductivity. This means that the structure of the membrane is to be selected concerning the arrangement of carriers and separate-active layers after this criterion. As high a proton conductivity as possible desired becomes natural.

It is favourable, if the separate-active layer is not in, essentially mixed proton-conductive and not conductive polymer ranges structured.

Excluded ones of the composition according to invention of the membrane are compositions, with which the block segments (A) and (B) imide structures and the block segment (B) direct sulfonic acid groups bound to an aromatic diamine component of the aromatic imide structure exhibits.

Further excluded of the composition according to invention is compositions, with which in the block segment (B) direct sulfonic acid groups bound at the aromatics are contained, those bottom respective Betriebsbzw. Operating conditions desulfonieren. This Desulfonierung steps in particular with deactivated aromatics, D. h. Aromatics with strong electron-pulling substituents/groups up. Z. B. desulfonieren sulfonic acid groups of supporting polyethersulfones, with which the sulfonic acid group direct at the aryl sulfone component (over sulfonic group coupled aromatics) bound is present, relative light in the aqueous system and/or. bottom Betriebs-bzw. Operating conditions in one Fuel cell. On the other hand no Desulfonierung of the sulfonic acid groups is, to Etherbaustein direct coupled are present, found.

The oligomeren block segments (A) consist favourable way of at least a Oligomersegment of the connecting classes Oligoarylimid and/or Oligoaryfensulfid and/or Oligoaryfsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligochinoxalin. That Degree of polymerization of the block segments (A) lies in range from 1 to 50, favourable-proves within the range of 4 to 30 and still favourable-proves between 5 and 10.

The block segment (B) exists thereby favourable-proves of at least a Oligomersegment of the connecting classes Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or

Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligochinoxalin and/or Oligoarylimid, excluded with this Oligoarylimid is present a direct sulfonic acid group bound at an aromatic amine component of an aromatic imide component and excluded in the block segment (B) is direct sulfonic acid groups, which desulfonieren in the membrane bottom operating conditions, with degrees of polymerization between 2 and 50, bound at the aromatics, whereby the Oligomersegmente as proton-conductive groups at least or a mixture at groups per Oligomereinheit of the type sulfonic acid and/or phosphonic acid and/or (perfluoros) alkyl-sulfone-acidic and/or (perfluoro) - alkyl phosphonic acid and/or (Perfluoro) alkyl carbonic acid possess.

An other favourable variant consists of the fact that the block segment (B) from at least a Oligomersegment of the connecting classes Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or

Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligoarylimid and/or Oligochinoxalin also

Degrees of polymerization between 2 and 50 and the proton-conductive Oligomersegmente of basic polymere-bound groups and low molecular and/or oligomeren compounds with acidic units of the type consist

Sulfonic acid and/or phosphonic acid and/or (perfluoro) - alkyl-sulfone-acidic and/or (Perfluor) alkyl phosphonic acid and/or (perfluoro) - exists alkyl carbonic acid, whereby the acid groups are contained compound (EN) over ionic interaction to the basic groups bound.

The block segment (B) can favourable-proves also from at least one

Oligomersegment of the connecting classes Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or

Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or

Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligoarylimid and/or Oligochinoxalin also

Degrees of polymerization between 2 and 50 and this Oligomersegmente consists of a mixture of chemical coupled oligomers exists at least, which oligomers with only basic oxidation-stable groups of the type triazine and/or tertiary Amino-und/or quaternary ammonium groups and oligomers with only acidic groups of the type sulfonic acid and/or phosphonic acid and/or (Perfluoros) - alkyl-sulfone-acidic and/or (perfluoros) - alkyl phosphonic acid and/or (perfluoro) - alkyl carbonic acid contains.

Favourable way knows the membrane in the separate-active layer neben'den Diund/or multi-block copolymers of other polymers and/or other additives to contain.

In favourable cases of the use of the membrane according to invention in a direct methanol fuel cell the block segment (A) works mainly to

Improvement of the mechanical stability and the methanol back attitude. That Block segment (B) is even proton-conductive and holds the methanol with higher Selectivity back.

A such membrane is favourable-proves from a block segment (A) out Oligoimid (EN) and/or Oligophenylensulfid (EN) and/or Oligosulfonamid (EN) and/or Oligoarylsulfon (EN) and/or Oligobenzimidazol (EN) and from one Block segment (B) from Oligophenylensulfid (EN) and/or Oligosulfonamid (EN) and/or Oligoarylsulfon (EN) and/or Oligobenzimidazol (EN) and/or Oligoimid (EN) with proton-conductive Sulfonsäure-und/or groups of phosphonic acids of constructed, excluded the block segments (A) and (B) exhibit imide structure and the block segment (B) exhibit direct sulfonic acid group bound to an aromatic diamine component of the aromatic imide structure, and point one

Structure A (B-A)_k with k = 2 to 10 up.

With the invention process to the production of a polymere Gas cell membrane, in particular a membrane, how it is other according to invention described above, starting materials used, which lead to block segments (A) with at least a electron-non conductive and a proton-non conductive Oligomersegment, become and which to block segments (B) with at least a proton-conductive and a electron-non conductive Oligomersegment lead.

At least one of the starting materials to the production of the block segment (A) and/or (B) is present as solution or as melt. The oligomeren block segments (A) and (B) with different in each case reactive end groups, which are for the coupling of the block segments (A) with the block segments (B) necessary, become first prepared in separated reactions. Both the block length and the type of the reactive end groups become certain by the composition of the starting materials. During the conversion of difunktionellen monomers of the general type CC with dd to the block segments the chain lengths of the block segments and the reactive functional end groups become by a defined excess of one of the monomers of the type CC or dd adjusted, like schematic in formula 1 shown. With the use of monomers of the type CD a difunktionelles monomer of the type CC and/or dd in a defined ratio to the component CD to the reaction given becomes the control of the chain length and the reactive functional end groups (see formula 2).

Formula 1 $n \text{ CC} + (n+1) \text{ Ddt (DD-CC)} n\text{-dd}$ (reactive functional end groups D)

Formula 2 $n \text{ CD} + \text{CC (CD)} n\text{-CC}$ (reactive functional end groups C)

A property according to invention of the block segments is also that those

Functionalities of its end groups only one coupling of the block segments (A) and (B) permit.

The block segments (B) become by conversion of monomers, those

Sulfonic acid (n) and/or phosphonic acid (n) and/or (perfluoro) - alkyl-sulfone-acidic (n) and/or (perfluoro) - alkyl phosphonic acid (n) and/or (perfluoro) - alkyl carbonic acid (n) and/or from

monomers, those contain at least of other protons a non conductive functional group such as z.
 B. Hydroxy groups contain, not to
 Structure of chain involved is and transfered by polymere-analogous conversions of the block segments to a proton-conductive group will can.

A criterion to the selection of the monomers to the production of a block segment (B), which can be used, is the density of the proton-conductive groups DPIG. defined through:

Number of the proton-conductive groups DPIG = #100%

Total number of the monomer units thereby should the density DPIG favourable-proves by addition of monomers without proton-conductive groups within the range of 20% to 200% adjusted to become.

Favourable way lies the group-dense between 50 and 100%. The degree of polymerization of the proton-conductive block segments (B) lies in range from 1 to 50, favourable-proves within the range of 1 to 30 and still favourable-proves between 2 and 10.

Further the oligomeren block segments (B) can by z. B. Sulfonation, Phosphonierung, conversion with A-halogen (by fluorine) alkyl-sulfone-acidic, A-halogen (by fluorine) alkyl phosphonic acids, A-halogen (by fluorine) alkyl carbonic acids, (with halogen fluorine) (Perfluor) alkylsultonen like z. B. Y-Propansulton, 6-Butansulton, or 1, 2, 2-Trifluor-2-hydroxy-1-trifluormethylethansulton (Perfluor) alkylactonen from the corresponding oligomeren block segments of the type (A) obtained become.

This method is particularly favourable, if the Oligomersynthese must take place in melt in addition, in solution with temperatures above 200 C.

Through brought together the separate reactions of the oligomeren

Block segments (A) and (B), whereby the different reactive functional

End groups C and D in an equimolar ratio are preferably present, become favourable-prove the multi-block copolymers of the general shape A (B-A) k obtained, whereby k favourable-proves values between can accept 2 and 10.

By this structure the finished membrane can do an as far as possible phaseseparated

Morphology with block segment (A) - rich phases (A-phase) and block segment (B) - rich phases (B-phase) and with essentially continuous proton conductivity obtained. Such proton-non conductive A-phases do not pour or only in a small periphery in waters and/or. Waters/methanol mixtures and essentially give the mechanical stability to the membranes. Further they form a barrier for waters and with the use of the membranes in DMFC for methanol between Anoden-und cathode compartment of a gas cell unit.

Over sourceabler B-phases of the membrane materials the made Protonenleitung between the anode and the cathode. The smaller mechanical stability conditional by the swelling becomes compensated by the A-phases. Apart from the Protonenleitung the B-phases in the operation in a DMFC essentially form a barrier for methanol between Anoden-und cathode compartment of a

gas cell unit.

Subsequent ones can become known Hilfs-und of additives and/or crosslinking agent added.

The swellable of the B-phase can become during or after the diaphragm production over the addition of crosslinking agents controlled.

After the formation Di-und according to invention/or multi-block copolymers this as separate-active layer (EN) alone or on and/or between and/or in a carrier as membrane formed become. whereby the membrane morphologic one

Structure with essentially continuous proton conductivity exhibits.

Favourable monomers for the production oligomere block segments (A) can be:

1. Oligoarylimid out

Benzophenontetracarbonsäuredianhydrid, Benzoltetracarbonsäuredianhydrid, 4, 4' (Hexafluorisopropyliden) - to phthalsäureanhydrid, 4, 4' - (isopropylidenes) - to phthalsäureanhydrid, Biphenyl-3, 3' - 4, 4' - tetracarbonsäuredianhydrid, 4, 4' - Oxy to phthalsäureanhydrid, Naphthalin-1, 4, 5, 8-tetracarbonsäuredianhydrid, and p-phenylene diamine, m phenylene diamine, 4, 4' - Diaminobiphenyl, 4, 4' - diaminodiphenyl ethers, 3, 3' - diaminodiphenyl ethers, 4, 4' - diaminodiphenylmethane, 1,5-Diaminonaphthalin, 1, 3-Diaminocyclohexan, 1, 4-Diaminocyclohexan, 4, 4' - diaminodiphenylsulfone, 2, 4-Diaminomesitylen, 3, 4' - Diaminobenzophenon, 4, 4' - Diaminobenzophenon, 4, 4' - Diaminodiphenylsulfid, 4, 4' - diaminodiphenylsulfone, 4, 4' - Diaminostilben, 2, 6-Diaminopyridin, 3, 5 Diaminopyridin, 2, 4-Diamino-4-hydroxybenzol, piperazine, 2, 4-Diaminopyrimidin, 4, 6-Diaminopyrimidin, 2, 4-Diamino-6-phenyl-1, 3, 5-triazin, 2, 4-Diamino-6-methyl-1, 3, 5-triazin, 4, 4' - Diamino octafluor biphenyl, 2, 4 toluene diisocyanate, 2, 6-Toluoldiisocyanat, 4, 4' - Methylendiphenylendiisocyanat, p phenylene diisocyanate, m-phenylene diisocyanate 2. Oligoarylsulfon from 2, 2-Bis (4-hydroxyphenyl) - propane, 2, 2-Bis (4-hydroxyphenyl) - by fluorine propane, 2, 2-Bis (4-hydroxyphenyl) - methane, until (4-hydroxyphenyl) - keton, 2, 2-Bis (4-hydroxyphenyl) - sulfide, 2, 2-Bis (4-hydroxyphenyl) - sulfone and until (4-Chlorphenyl) - sulfone, until (4-Fluorphenyl) - sulfone

3. Oligoaramid out

Terephthalic acid, isophthalic acid, Naphthalin-1, 4-dicarbonsäure, Naphthalin-1, 5 dicarbonic acid, Naphthalin-2, 6-dicarbonsäure, Diphenylsulfon-4, 4' - dicarbonic acid, Biphenyl-4, 4' - dicarbonic acid, Diphenylether-4, 4' - dicarbonic acid, Cyclohexan-1, 4 dicarbonic acid, 2, 6-Pyridindicarbonsäure, 5-Hydroxyisophthalsäure, Aminobenzoe acidic and p-phenylene diamine, m phenylene diamine, 4, 4' - Diaminobiphenyl, 4, 4' - Diaminodiphenyl ether, 3, 3' - diaminodiphenyl ethers, 4, 4' - diaminodiphenylmethane, 1, 5-Diamino naphthalin, 1, 3-Diaminocyclohexan, 1, 4-Diaminocyclohexan, 4, 4' - Diaminodiphenyl sulfone, 2, 4-Diaminomesitylen, 3, 4' - Diaminobenzophenon, 4, 4' - Diaminobenzophenon, 4, 4' - Diaminodiphenylsulfid, 4, 4' - diaminodiphenylsulfone, 4, 4' - Diaminostilben, 2, 6-Diaminopyridin, 3, 5 Diaminopyridin, piperazine, 2, 4-Diamino-pyrimidin, 4, 6-Diaminopyrimidin, 2, 4-Diamino-6-phenyl-1, 3, 5-triazin, 2, 4-Diamino-6-methyl-1, 3, 5-triazin, 4,

4,4'-Diamino octafluorobiphenyl 4. Oligoarylharnstoff from p-phenylene diamine, m-phenylene diamine, 4,4'-Diaminobiphenyl, 4,4'-diaminodiphenyl ethers, 3,3'-diaminodiphenyl ethers, 4,4'-diaminodiphenylmethanes, 1,5-Diaminonaphthalin, 1,3-Diaminocyclohexan, 1,4-Diaminocyclohexan, 4,4'-diaminodiphenylsulfone, 2,4-Diaminomesitylen, 3,4'-Diaminobenzophenon, 4,4'-Diaminobenzophenon, 4,4'-Diaminodiphenylsulfid, 4,4'-diaminodiphenylsulfone, 4,4'-Diaminostilben, 2,6-Diaminopyridin, 3,5-Diaminopyridin, piperazine, 2,4-Diamino-pyrimidin, 4,6-Diaminopyrimidin, 2,4-Diamino-6-phenyl-1,3,5-triazin, 2,4-Diamino-6-methyl-1,3,5-triazin, 4,4'-Diamino octafluorobiphenyl and 2,4-Toluylendiisocyanat, 2,6-Toluylendiisocyanat, 4,4'-Methylen-diphenylendiisocyanat, p-phenylene diisocyanate, m-phenylene diisocyanate 5. Oligoarylsulfonamid from Benzol-1,3-disulfonsäure, Benzol-1,4-disulfonsäure, Naphthalin-1,5-disulfonsäure, Naphthalin-2,6-disulfonsäure and p-phenylene diamine, m-phenylene diamine, 4,4'-Diaminobiphenyl, 4,4'-Diaminodiphenyl ether, 3,3'-diaminodiphenyl ethers, 4,4'-diaminodiphenylmethane, 1,5-Diamino naphthalin, 1,3-Diaminocyclohexan, 1,4-Diaminocyclohexan, 4,4'-Diaminodiphenyl sulfone, 2,4-Diaminomesitylen, 3,4'-Diaminobenzophenon, 4,4'-Diaminobenzophenon, 4,4'-Diaminodiphenylsulfid, 4,4'-diaminodiphenylsulfone, 4,4'-Diaminostilben, 2,6-Diaminopyridin, 3,5-Diaminopyridin, piperazine, 2,4-Diamino-pyrimidin, 4,6-Diaminopyrimidin, 2,4-Diamino-6-phenyl-1,3,5-triazin, 2,4-Diamino-6-methyl-1,3,5-triazin, 4,4'-Diamino octafluorobiphenyl

6. Oligobenzimidazol out
Terephthalic acid, isophthalic acid, Naphthalin-1,4-dicarbonsäure, Naphthalin-1,5-dicarbonsäure, Naphthalin-2,6-dicarbonsäure, Diphenylsulfon-4,4'-dicarbonic acid, Biphenyl-4,4'-dicarbonic acid, Diphenylether-4,4'-dicarbonic acid, Cyclohexan-1,4-dicarbonic acid, Pyridin-2,6-dicarbonsäure, 5-Hydroxyisophthalsäure and 3,3',4,4'-Tetraaminobiphenyl, 3,3',4,4'-Tetraaminodiphenylether, 3,3',4,4'-tetraaminobenzophenon, 3,3',4,4'-Tetraaminodiphenylsulfid, 3,3',4,4'-Tetraaminodiphenylsulfon, 1,2,4,5-Tetraaminobenzol, 3,3',4,4'-Tetraaminodiphenylenoxid, 1,2,5,6-Tetraaminoanthrachinon, 2,3,6,7-Tetraaminophenazin 7. Oligobenzoxazol from terephthalic acid, isophthalic acid, Naphthalin-1,4-dicarbonsäure, Naphthalin-1,5-dicarbonsäure, Naphthalin-2,6-dicarbonsäure, Diphenylsulfon-4,4'-dicarbonic acid, Biphenyl-4,4'-dicarbonic acid, Diphenylether-4,4'-dicarbonic acid, Cyclohexan-1,4-dicarbonsäure, 5-Hydroxyisophthalsäure and 2,5-Diamino-1,4-benzoldiol (2,5-Diaminohydrochinon), 4,6-Diamino-1,3-benzoldiol (4,6-Diaminoresorcin) 8. Oligobenzothiazol from terephthalic acid, isophthalic acid, Naphthalin-1,4-dicarbonsäure, Naphthalin-1,5-dicarbonsäure, Naphthalin-2,6-dicarbonsäure, Diphenylsulfon-4,4'-dicarbonic acid, Biphenyl-4,4'-dicarbonic acid, Diphenylether-4,4'-dicarbonic acid, Cyclohexan-1,4-dicarbonsäure, Pyridin-2,6-dicarbonsäure, 5-Hydroxyisophthalsäure and 2,5-Diamino-1,4-benzoldithiol, 4,6-Diamino-1,3-benzoldithiol

9. Oligochinoxalin from Bisglyoxaldihydrate of: 1,3-Diacetylbenzol, 1,4-Diacetylbenzol, 4,4'-Diacetyl-biphenyl, 4,4'-Diacetyldiphenylether, 4,4'-Diacetyldiphenylsulfid, 4,4'-Diacetyldiphenylsulfon, 4,4'-Diacetyldiphenylmethan and/or. the corresponding Until (phenyl A diketone) and 3,3',4,4'-Tetraaminobiphenyl, 3,3',4,4'-

Tetraaminodiphenylether, 3, 3', 4, 4' - Tetraaminobenzophenon, 3, 3', 4, 4' -
 Tetraaminodiphenylsulfid, 3, 3', 4, 4' - Tetraaminodiphenylsulfon, 1, 2, 4, 5-Tetraaminobenzol,
 3, 3', 4, 4' - Tetraaminodiphenylenoxid, 1, 2, 5, 6, - Tetraaminoanthrachinon, 2, 3, 6, 7-
 Tetraaminophenazin favourable monomers, which lead only to the production of the oligomeren
 block segments (B), additional to for the production of the block segments (A) specified, can be:

1. Oligoarylimid from 3,5-Diaminobenzoessäure, 2, 4-Diamino-phenylen-4 (butyloxy-4-sulfonsäure), 2,4Diamino-phenylen-4 (propyloxy-3-sulfonsäure), 2, 4-Diamino-phenylen-4 (perfluorisopropyloxy-2-sulfonsäure)
2. Oligoarylenether from 3, 5-Dihydroxybenzoessäure, 2,6-Dihydroxybenzoessäure, 2, 5-Dihydroxy-1, 4-benzoldisulfonsäure, 2, 5-Dihydroxy-1, 3-benzoldisulfonsäure
3. Oligoaramid from 5-Isophthalphosphonsäure, 5-Isophthalsulfonsäure, Terephthalsulfonsäure, p-Phenylendiaminsulfonsäure, m phenylene-diamine-sulfone-acidic, 4, 4' - Diaminobiphenyl 2, 2' - disulfonsäure, 4, 4' - Diaminostilben-2, 2' disulfonsäure, 2, 4-Diaminomesitylen-6sulfonsäure, 3,5-Diaminobenzoessäure
4. Oligoarylarnstoff from p-Phenylendiaminsulfonsäure, m phenylene-diamine-sulfone-acidic, 4, 4' - Diaminobiphenyl 2, 2' - disulfonsäure, 4, 4' - Diaminostilben-2, 2' disulfonsäure, 2, 4-Diaminomesitylen-6 sulfone-acidic, 3,5-Diaminobenzoessäure, 2, 4-Diamino-phenylen-4 (butyloxy-4-sulfon acidic), 2, 4-Diamino-phenylen-4 (propyloxy-3-sulfonsäure), 2, 4-Diamino-phenylen-4 (perfluorisopropyloxy-2-sulfonsäure)
5. Oligoarylsulfonamid from p-Phenylendiaminsulfonsäure, m phenylene-diamine-sulfone-acidic, 4, 4' - Diaminobiphenyl 2, 2' - disulfonsäure, 4, 4' - Diaminostilben-2, 2' disulfonsäure, 2, 4-Diaminomesitylen-6 sulfone-acidic, 3,5-Diaminobenzoessäure, 2, 4-Diamino-phenylen-4 (butyloxy-4-sulfon acidic), 2, 4-Diamino-phenylen-4 (propyloxy-3-sulfonsäure), 2, 4-Diamino-phenylen-4 (perfluorisopropyloxy-2-sulfonsäure)
6. Oligobenzimidazol from 5-Isophthalphosphonsäure, 5-Isophthalsulfonsäure, Terephthalsulfonsäure
7. Oligobenzoxazol from 5-Isophthalphosphonsäure, 5-Isophthalsulfonsäure, Terephthalsulfonsäure
8. Oligobenzothiazol from 5-Isophthalphosphonsäure, 5-Isophthalsulfonsäure, Terephthalsulfonsäure

combinations of the monomers within a block segment (A) and/or (B) are possible. The criterion to the selection of the monomers and their combinations are the 1 according to claim to reaching properties of the block segments (A) and (B).

For the synthesis of the oligomeren block segments (A) and (B) become carbonsäure-und the sulfone-acidic monomers favourable-proves as acid chlorides used. In addition, the carbon-acidic monomers can become as methyl or Phenylester used. Furthermore it is favourable, the revision modification NO, to silylieren Thiol and hydroxy groups, which are at the Oligomerbildung involved.

Hydroxy groups exhibiting monomers can become in form of their acetates used.

The conversion that monomers to the oligomeren block segments (A) and (B) as well as the

production Di-und/or multi-block copolymers made in solution or in melt, whereby at least one of the used monomers in solution or in Melt is present.

For the reactions, which become conducted in solution, become in particular polar aprotic solvents as for example dimethylformamide (DMF), Dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), tetrahydrofurane (THF), 1,4 Dioxan or N-methylpyrrolidone (NMP) used. If necessary become these Solvents up to 5 mA. - % low molecular salts, like lithium chloride or Calcium chloride added, around the solubility that oligomers in the corresponding To increase solvents. The ratio solvent/monomers becomes a so selected that Oligomer and late Di-und/or MultiBtöpkcopotymerkonzentration in the range between 5 and 30 mA. - %, preferably, between 10 and 20 mA. - is appropriate for %. These solutions become used after a filtration by ei'be glass frit and if necessary by addition of other polymers and/or other additives the production of the membranes. Di-und/or Multi block copolymer concentration of these solutions becomes so adjusted that those Solutions a viscosity favourable for the production of the membranes exhibit.

The viscosity attitude can take place also via partial evaporation of the solvent in the vacuum or via addition from solvent.

Possibilities to the production of membranes according to invention are the subsequent:

1. To the production of self-supporting separate-active layers, D. h. such membranes without additional carriers, are contained solutions, those at least one the-or of the multi-block copolymers according to invention or of solutions, those at least a oligomeres block segment (A) and at least a oligomeres Block segment (B) or solutions, those at least a oligomeres block segment (A) and/or at least a oligomeres block segment (B) and at least the-or multi-block copolymer contain, with the help of doctor blades to a film with a thickness of 100-500 over on an inert, smooth support z. B. from glass, Ptfе or stainless steel processed. Forwards and/or during and/or after that Film formation finds the coupling of the oligomeren block segments (A) and (B) and/or or the-or the multi-block copolymers to Di-und/or Multi-block copolymers instead of. The solvent becomes subsequent complete in the vacuum or same complete in the vacuum evaporated, first partial at air, by energy input either, and. The temperatures for it lie in Range of 50-150 C. The so obtained dry membranes exhibit thickness from 50 to 150 pm, preferably between 60 and 100 over, whereby the thickness of the membranes of the thickness of the taken off polymer film and that Polymer concentration dependent is. The membranes point a phaseseparated morphology with essentially more continuous Proton conductivity up.

2. The production of membranes with an separate-active layer applied on a carrier first the support material, which consists of a porous or a textile material, becomes for example from polyphenylene oxide or Polyphenylene sulfide, on an inert, smooth support z. B. from glass, ptfe or Stainless steel placed or fixed. The application of the separate-active layer becomes, like bottom 1. Described ones, proceed. The separate-active layer on the carrier points a phaseseparated morphology with essentially more continuous Proton conductivity up.
3. The production of membranes with an separate-active layer introduced in a carrier the support material, which consists of a porous or a textile material, becomes for example from polyphenylene oxide or Polyphenylene sulfide, with Di-und/or multi-block copolymer contained Solution impregnated. By evaporation of the solvent, like bottom 1.

Described one, becomes the membrane obtained. The separate-active layer, itself into that Voids of the carrier, exhibits a phaseseparated morphology with essentially continuous proton conductivity finds.

4. To the production of membranes with an separate-active layer between two Support materials first a polymer film becomes on a support material as more bottom 2. described applied. Before the evaporation of the solvent a second support material becomes applied on this polymer film. The completion of these Membrane by evaporation of the solvent made, like bottom 1. beschrieben.

The separate-active layer between the carriers points a phaseseparated Morphology with essentially continuous proton conductivity up.

5. The production of membranes with more than an separate-active layer one becomes Membrane, which became after one of the possibilities 1 to 4 prepared, with an other polymer solution coated, which can contain same or another those and/or multi-block copolymer. The completion of the membrane by evaporation of the solvent made as in 1. described. The additional (n) separate-active (n) layer (EN) on the carrier points a phaseseparated morphology with essentially more continuous Proton conductivity up.

In the other the invention at several embodiments is more near explained.

Comparison example 1

A Nafion membrane (DuPont) becomes used as standard diaphragm for DMFC. In To methanol water solutions (5 mass % methanol) this membrane and it pour stop themselves the diaphragm characteristics. With a proton conductivity of 0,2 S/cm with 80 C a sufficient

conductivity becomes achieved. The barrier property of Nafion membranes with a methanol permeability of 30% and more is not for an application in DMFC suitable.

Example 1 1 production of the oligomers block segment A1: In 200 ml dried 1-Methyl-2-pyrrolidon [NMP] 0.1 mol of Dibenzophenontetracarbonsäuredianhydrid with 0,04 mol of Toluyldiamin reacted becomes in pure sp nitrogen atmosphere bottom agitation. After 1 hour agitation with 120 C 0, 04 mol becomes 4, 4' - diaminodiphenyl ethers added and an other hour agitated. Afterwards slow 0.2 mol acetic anhydride is course-dripped with 120 C. After the addition will still 1 hour agitated and subsequent becomes the solution bottom agitation on 160 C heated and the acetic acid abdestilliert reaction solution A1 (anhydride-terminated).

Block segment a2:

In 200 ml dried 1-Methyl-2-pyrrolidon [NMP] bottom inert becomes Conditions (pure sp nitrogen atmosphere) bottom agitations 0.08 mol Dibenzophenontetracarbonsäuredianhydrid with 0,05 mol of Toluyldiisocyanat and 0.05 mol of Methylendiphenylendiisocyanat reacted and an hour with 140 C agitated. Afterwards the solution slow bottom agitation becomes short heated on 180 C Reaction solution a2 (isocyanate-terminated)

Block segment A3:

In 200 ml dried 1-Methyl-2-pyrrolidon [NMP], the 3 mA. - In pure sp nitrogen atmosphere bottom agitation 0.1 mol contains, becomes % LiCl (more sophthalsäuredimethylester with 0,04 mol of Toluyldiamin reacted. After 1 hour Agitation with 120 C 0.04 mol of 4, 4' - diaminodiphenyl ethers added and an other hour agitated become. Subsequent one becomes the solution bottom agitation 15 min on 160 C warming up reaction solution A3 (ester-terminated).

Block segment A4: In melt 0.09 mol becomes Bistrimethylsilyl bisphenol A with 0, 1 mol of 4, 4' - difluordiphenylsulfon bottom addition of catalytic quantities CsF with temperatures within the range of 250 and 300 C bottom elimination of the Trimethylsilylfluorids reacted in pure sp nitrogen atmosphere bottom agitation. After 1 hour agitation 0.02 mol at silylated 4-Hydroxybenzoesäureethylester added and an other hour agitated becomes. Subsequent one becomes the oligomer in 200 ml NMP dissolved reaction solution A4 (ester-terminated).

Block segment A5: Bottom pure sp nitrogen atmosphere to 200 ml dried NMP with 0,08 mol until trimethylsilyl m phenylendiamin bottom agitations 0, 1 mol of Benzol-1, 3disulfonsäuredichlorid in NMP slow is course-dripped. The solution becomes 8 hours with 100 C agitating reaction solution A5 (sulfone-acidic-chloride-terminated).

Block segment B1: Bottom pure sp nitrogen atmosphere become in 200 ml dried NMP, the 3 mA. , Bei-18 C contains % LiCl to 0.1 mol trichloroethylene trimethylsilyl p phenylendiaminsulfonsäure 0.08 mol of Isophthalsäuredichlorid added and an hour bei-18 C as well as 8

Hours with 100 C bottom agitations reacted. - Reaction solution B1 (amine-terminated).

Block segment B2:

Bottom pure sp nitrogen atmosphere become 200 ml dried NMP, the 3

MA. -, With 0, 1 mol trichloroethylene trimethylsilyl p phenylendiaminsulfonsäure contains % LiCl more bottom

Agitation 0, 08 mol of Toluylendiisocyanat in NMP slow course-drips. After addition of catalytic quantities at dibutyltin oxide the solution becomes 8 hours with 50 C agitated - reaction solution B2 (amine-terminated).

Block segment B3:

Unter Reinst-Stickstoff-Atmosphäre werden zu 200 ml getrocknetem NMP mit 0,1 mol Tris-trimethylsilyl-p-phenylendiaminsulfonsäure unter Rühren 0,08 mol Benzol

1, 3-disulfonsäuredichlorid in NMP slow course-drips. The solution becomes 8 hours with 100 C agitating reaction solution B3 (amine-terminated).

2 production of the membranes block copolymer membrane 1: To the reaction solution A1 the slow reaction solution B1 bottom agitation is course-dripped. After 1 hour agitation with 120 C 0, 05 mol acetic anhydride is course-dripped and 1 hour other-agitated. Bottom vacuums and the solution concentrated is taken off to agitation and to a membrane and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 1/20 the Nafion Vergleichsmembran block copolymer membrane 2: To the reaction solution a2 the slow reaction solution B1 bottom agitation is course-dripped. After 1 hour agitation with 120 C becomes bottom vacuums and agitation the solution concentrated and on a Polyphenylensulfid Trägervlies applied and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 7/100 the Nafion Vergleichsmembran

Block copolymer membrane 3:

To the reaction solution A3 the slow reaction solution B1 bottom agitation is course-dripped.

After 1 hour agitation with 130 C becomes bottom vacuums and agitation those

Solution concentrated and to a membrane taken off and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 2/100 the Nafion Vergleichsmembran

Block copolymer membrane 4:

To the reaction solution A1 the slow reaction solution B2 bottom agitation is course-dripped.

After 8 hour agitation with 130 C becomes bottom vacuums and agitation those

Solution so concentrated that the solution moistening in a fine

Glass fiber fabric introduced and bottom vacuums slow dried becomes. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 3/100 the Nafion Vergleichsmembran block copolymer membrane 5:
To the reaction solution A4 the slow reaction solution B3 bottom agitation is course-dripped.
After 8 hours agitation with 130 C is taken off bottom vacuums and to agitation the solution concentrated and to a membrane and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 1/100 the Nafion Vergleichsmembran block copolymer membrane 6:
The reaction solution A5 added becomes the reaction solution B3 bottom agitation.

After 8 hours agitation with 130 C will become the solution cooled and it 0.01 mol of Diandiglycidether as crosslinking agent added. The solution is taken off immediately to the membrane, bottom vacuums dried and 5 hours with 100 C tempered. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 2/100 the Nafion Vergleichsmembran
Block copolymer membrane 7:
The reaction solution A5 added becomes the reaction solution B3 bottom agitation.

After 8 hours agitation with 130 C will become the solution cooled and it 0.01 mol of 4, 4' - Difluordiphenylsulfon as crosslinking agent added. The solution becomes
Membrane taken off, bottom vacuums dried and 8 hours with 120 C tempered. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 5/100 the Nafion Vergleichsmembran
Block copolymer membrane 8: To 50 ml reaction solution a2 and 50 ml reaction solution A4 are course-dripped slow 100 ml the reaction solution B3 bottom agitation. After 8 hours agitation with 130 C is taken off bottom vacuums and to agitation the solution concentrated and to a membrane and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 1/100 the Nafion Vergleichsmembran block copolymer membrane 9:
To 100 ml reaction solution A1 slow 50 is course-dripped ml the reaction solution B1 and 50 ml the reaction solution B3 bottom agitation. After 8 hours agitation with 130 C is taken off bottom vacuums and to agitation the solution concentrated and to a membrane and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 4/100 the Nafion Vergleichsmembran block copolymer membrane 10: To 100 mi reaction solution A1 slow 45 is course-dripped ml the reaction solution B1 and 45 mi of the reaction solution B3 bottom agitation. After 8 hours agitation with 130 C is taken off bottom vacuums and to agitation the solution concentrated and to a membrane and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 9/100 the Nafion Vergleichsmembran Block copolymer membrane 11: To 90 ml reaction solution A1 slow 50 is course-dripped ml the reaction solution B2 and 50 ml the reaction solution B3 bottom agitation. After 8 hours agitation with 130 C is taken off bottom vacuums and to agitation the solution concentrated and to a membrane and bottom vacuums slow dried. It becomes a good manageable, mechanical stable membrane obtained.

Methanol retention ability: 7/100 the Nafion Vergleichsmembran

[Claims of WO03030289](#)[Print](#)[Copy](#)[Contact Us](#)[Close](#)

Result Page

Notice: This translation is produced by an automated process; it is intended only to make the technical content of the original document sufficiently clear in the target language. This service is not a replacement for professional translation services. The esp@cenet® Terms and Conditions of use are also applicable to the use of the translation tool and the results derived therefrom.

Claims

1. Polymers gas cell membrane, from at least an separate-active Layer or at least a carrier and at least an separate-active layer exist, whereby the separate-active (n) layer (EN) on and/or between and/or in the carrier is/is applied, and whereby the separate-active (n) layer (EN) at least from Di-und/or multi-block copolymers with the general segment structures A (B-A) k and/or B (A-B), and/or (A-B) m with k ≥ 1 and 1 ≥ 1 and m ≥ 1 exists, in which the block segment (A) consists electrons of at least a non conductive and proton-non conductive Oligomersegment, and which Block segment (B) from at least a proton-conductive and electrons non conductive Oligomersegment exists and the membrane morphologic one Structure with essentially continuous proton conductivity exhibits and excluded the block segments (A) and (B) exhibits imide structure and that Block segment (B) exhibits direct sulfonic acid groups bound to an aromatic diamine component of the aromatic imide structure and excluded in the block segment (B) is direct sulfonic acid groups bound at the aromatics, which desulfonieren in the membrane bottom operating conditions.
2. Membrane according to claim 1, with which the block segment (A) consists of at least a Oligomersegment of the connecting classes Oligoarylimid and/or Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligochinoxalin with degrees of polymerization between 2 and 50.
3. Membrane according to claim 1, with that the block segment (B) from at least a Oligomersegment of the connecting classes Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligochinoxalin and/or Oligoarylimid, with

degrees of polymerization between 2 and 50 exists, whereby the Oligomersegmente as Proton-conductive groups at least or a mixture at groups per Oligomereinheit of the type sulfonic acid and/or phosphonic acid and/or (perfluoro) Alkyl-sulfone-acidic and/or (perfluoros) - alkyl phosphonic acid and/or (perfluoro) Alkyl carbonic acid possess.

4. Membrane according to claim 1, with that the block segment (B) from at least one Oligomersegment of the connecting classes Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligoarylimid and/or Oligochinoxalin also Degrees of polymerization between 2 and 50 exists and the proton-conductive Oligomersegmente from basic polymere-bound groups and low molecular and/or oligomeren compounds with acidic units of the type sulfonic acid and/or phosphonic acid and/or (perfluoro) - alkyl-sulfone-acidic and/or (Perfluor) alkyl phosphonic acid and/or (perfluoro) - exists alkyl carbonic acid, whereby the acid groups are contained compound (EN) over ionic interaction to the basic groups bound.

5. Membrane according to claim 1, with which the block segment (B) from at least a Oligomersegment of the connecting classes Oligoarylsulfid and/or Oligoarylsulfon and/or Oligoarylethersulfon and/or Oligoarylenether and/or Oligoaryletherketon and/or Oligoarylenetheretherketon and/or Oligoaramid and/or Oligoarylharnstoff and/or Oligoarylenoxadiazol and/or Oligoarylsulfonamid and/or Oligobenzimidazol and/or Oligobenzoxazol and/or Oligobenzthiazol and/or Oligoarylimid and/or Oligochinoxalin with degrees of polymerization between 2 and 50 exists and this Oligomersegmente at least of a mixture of chemical coupled oligomers consist, which oligomers with only basic oxidation-stable groups of the type Triazinund/or tertiary Amino-und/or quaternary ammonium groups and oligomers with only acidic groups of the type sulfonic acid and/or phosphonic acid and/or (Perfluoros) - alkyl-sulfone-acidic and/or (perfluoros) - alkyl phosphonic acid and/or (perfluoro) - alkyl carbonic acid contains.

6. Membrane according to claim 1 that in the separate-active layer beside the those and/or multi-block copolymers other polymers and/or other additives are contained.

7. Membrane according to claim 1, with that the separate-active layer in, essentially mixed proton-conductive and not conductive polymer ranges structured is not.

8. Membrane according to claim 1, with which Di-und is/or multi-block copolymers linear or branched formed.

9. Membrane according to claim 1, with that the carrier from a porous or a textile Material exists.
10. Membrane according to claim 1, with which the block segment (A) consists of same or various Oligomereinheiten.
11. Membrane according to claim 1, with which the block segment (B) consists of same or various Oligomereinheiten.
12. Membrane according to claim 1, with which the length of the block segments (B) is a corresponding optimum proton conductivity selected.
13. Membrane according to claim 1, with which the block segment (A) from Oligoimid (EN) and/or Oligophenylensulfid (EN) and/or Oligosulfonamid (EN) and/or Oligoarylsulfon (EN) and/or Oligobenzimidazol (EN) and the Blocksegment' (B) from Oligoimid (EN) and/or Oligophenylensulfid (EN) and/or Oligosulfonamid (EN) and/or Oligophenylensulfon (EN) and/or Oligophenylethersulfon (EN) and/or Oligobenzimidazol (EN) and/or Oligochinoxalin (EN) with proton-conductive Sulfonsäure-und exists/or groups of phosphonic acids and which structure A (B-A) exhibits k with $k = 2$ to 10.
14. Method to the production of a polymere gas cell membrane, with to the production of the block segments (A) from at least electrons a non conductive and proton-non conductive Oligomersegment and with to
Production of the block segments (B) from at least a proton-conductive and
Electron-non conductive Oligomersegment the starting materials to the reaction brought becomes, whereby at least one of the starting materials in solution or as
Melt is present and whereby the block segments become separated prepared, whereby the functionalities of the end groups only one coupling of (A) with (B) and subsequent Di-und makes possible/or multi-block copolymers for the general
Segment structures A (B-A) k and/or B (A-B), and/or (A-B) m with $k > 1$ and $I \geq 1$ and $m \geq 1$ by reactive conversion prepared becomes, whereby subsequent known Hilfs-und of additives and/or crosslinking agent added to become to be able and Di-und/or multi-block copolymers as separate-active layer (EN) alone or on and/or between and/or in a carrier as membrane formed become, whereby the membrane exhibits a morphologic structure with essentially continuous proton conductivity.
15. Process according to claim 14, selected with which over the choice of the starting materials the type, amount and functionality of the block segments and their end groups and segment structures become.
16. Process according to claim 14, with which after the mixture of the block segments the reactive conversion becomes Di-und/or multi-block copolymers on and/or between and/or in/the

support material/ien conducted.

17. Process according to claim 14, with after the mixture of the block segments the reactive conversion to Di-und/or multi-block copolymers during and/or after the diaphragm production made.

18. Process according to claim 14, with during and/or after the diaphragm production a crosslinking by means of jets high-energy and/or chemical agents the made.